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Key indicators

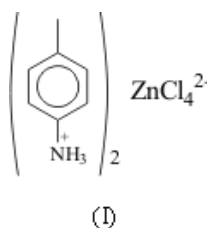
Single-crystal X-ray study
 $T = 280\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.044
 wR factor = 0.106
Data-to-parameter ratio = 29.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(*p*-toluidinium) tetrachlorozincate(II)

The title organic–inorganic hybrid salt, bis(*p*-toluidinium) tetrachlorozincate(II), $(\text{C}_7\text{H}_7\text{NH}_3)_2[\text{ZnCl}_4]$, crystallizes in a structure consisting of alternating ionic and organic layers. Weak $\text{C}-\text{H}\cdots\pi$ hydrogen-bonding interactions occur in the organic layer, and strong charge-assisted $\text{N}-\text{H}\cdots\text{Cl}$ interactions are present in the inorganic layer between ammonium groups and discrete $[\text{ZnCl}_4]^{2-}$ tetrahedra.

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Comment

The structure determination of the title compound, (I), is part of an ongoing investigation of the structures of and non-covalent interactions present in self-assembling organic–inorganic hybrid materials prepared by the combination of an organic cation and perhalometallate anion. The structures of only two organic–inorganic hybrid materials containing only *p*-toluidinium cations and perhalometallate anions have been reported in the literature, namely *p*-toluidinium hexachlororhenate(IV) (Adman & Margulis, 1976) and *catena*-poly[bis(*p*-toluidinium) μ_2 -chloro-tetrachlorothallate(III)] (James *et al.*, 1996), both of which have a different ratio of cations to anions compared with the title compound, (I).



The molecular geometry of (I), as well as the atom-numbering scheme, are illustrated in Fig. 1. The asymmetric unit contains one inorganic tetrachlorozincate(II) anion and two crystallographically inequivalent organic *p*-toluidinium cations (cation 1 containing atom N1 and cation 2 containing atom N2). As illustrated in Fig. 2, the crystal structure is comprised of alternating organic and inorganic sheets parallel to the (010) plane of the unit cell. The organic layer contains the aromatic and methyl groups, whereas the ammonium groups and isolated tetrachlorozincate(II) anions form the inorganic layer.

The molecular packing results in an interdigitated organic layer, with cations packing in inversion-related pairs, and with the molecular planes of cation 1 (r.m.s. deviation of 0.0237 Å) and cation 2 (r.m.s. deviation of 0.0062 Å) inclined at angles of 86.56 (8) and 86.40 (8)°, respectively, relative to the (010) plane. An angle of 48.29 (13)° is formed between the two cation molecular planes. No intermolecular π – π interactions are evident in this layer, the shortest centroid-to-centroid

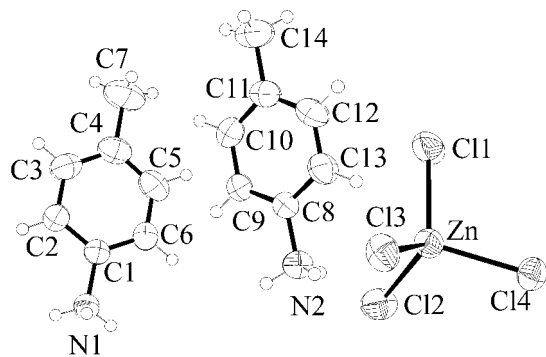


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level.

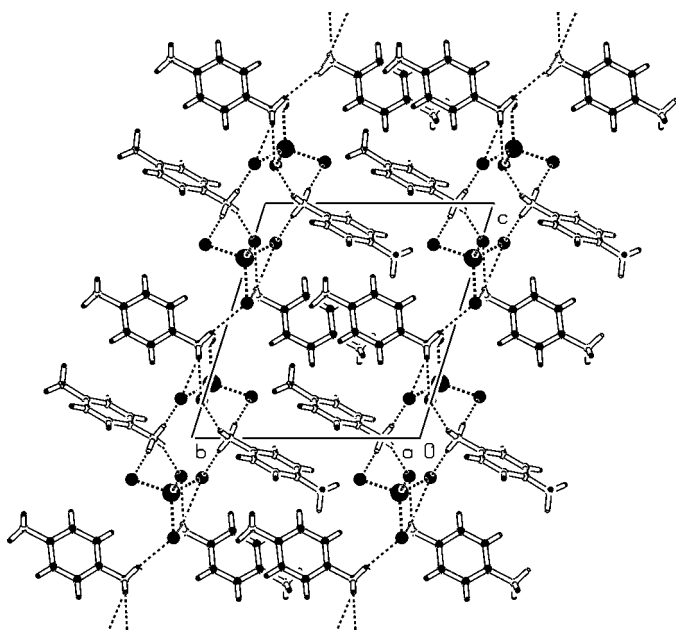


Figure 2
Packing diagram for (I), viewed down the *a* axis, showing the layered packing and hydrogen-bonding (dashed lines) interactions in the inorganic layer.

distance being 4.155 (5) Å. However, C—H... π hydrogen-bond interactions are present, with methyl atom C14 interacting with the aromatic group C1–C7 (symmetry code: $2 - x, 1 - y, 1 - z$), through atom H14B ($H \cdots \pi = 3.11$ Å), and through atom H14A with aromatic group C8–C14 (symmetry code: $1 - x, 1 - y, 1 - z$) ($H \cdots \pi = 2.97$ Å). In the inorganic layer, the $[ZnCl_4]^{2-}$ anions display a slightly distorted tetrahedral geometry, with Zn—Cl bond lengths in the range 2.2386 (18)–2.2828 (18) Å and Cl—Zn—Cl angles in the range 106.91 (7)–112.49 (7)°.

It has been shown that Cl atoms coordinated to metal-atom centres are good hydrogen-bonding acceptors (Aullon *et al.*, 1998). In (I), a two-dimensional hydrogen-bonding network of charge-assisted N—H...Cl interactions is established between tetrahedral tetrachlorozincate(II) anions and ammonium groups. The two crystallographically independent cations display different hydrogen-bonding interactions. Atom N1 in

cation 1 participates in three normal hydrogen bonds to three Cl acceptor atoms in three different $[ZnCl_4]^{2-}$ tetrahedra. The ammonium group in cation 2 forms two normal and one bifurcated hydrogen bond to four Cl acceptor atoms in three different tetrahedra. Hydrogen-bonding parameters are listed in Table 1 and the resulting hydrogen-bonding network in the inorganic layer is illustrated in Fig. 2.

Experimental

p-Toluidinium chloride was prepared by the dropwise addition of concentrated hydrochloric acid (8 ml, 37%, Aldrich) to a solution of *p*-toluidine (1.6 g, 99%, Aldrich) in chloroform (40 ml, 99%, Saarchem). The resulting precipitate was filtered off and dried in air. The title compound was crystallized by slow evaporation of an aqueous solution (40 ml) of *p*-toluidinium chloride (0.3590 g, 0.25 mmol) and $ZnCl_2$ (0.1704 g, 0.125 mmol, 96%, Saarchem) (2:1 ratio) at room temperature. A needle-like dark-brown crystal was selected for the X-ray diffraction study and was cut to an appropriate size.

Crystal data

$(C_7H_7NH_3)_2[ZnCl_4]$
 $M_r = 423.35$
Triclinic, $P\bar{1}$
 $a = 7.119$ (8) Å
 $b = 11.532$ (6) Å
 $c = 12.490$ (7) Å
 $\alpha = 107.14$ (5)°
 $\beta = 95.43$ (7)°
 $\gamma = 92.03$ (6)°
 $V = 973.3$ (13) Å³

$Z = 2$
 $D_x = 1.445$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 195 reflections
 $\theta = 2$ –31°
 $\mu = 1.81$ mm⁻¹
 $T = 280$ (2) K
Block, dark brown
0.30 × 0.20 × 0.20 mm

Data collection

Oxford Excalibur2 diffractometer
 ω scans
Absorption correction: multi-scan (Blessing, 1995)
 $T_{min} = 0.601$, $T_{max} = 0.700$
9806 measured reflections
5949 independent reflections

3404 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.033$
 $\theta_{max} = 31.7^\circ$
 $h = -10 \rightarrow 7$
 $k = -16 \rightarrow 16$
 $l = -17 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.106$
 $S = 0.90$
5949 reflections
202 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.005$
 $\Delta\rho_{max} = 0.61$ e Å⁻³
 $\Delta\rho_{min} = -0.71$ e Å⁻³

Table 1
Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...Cl1 ⁱ	0.89	2.29	3.171 (4)	172
N1—H1B...Cl4 ⁱⁱ	0.89	2.42	3.275 (3)	161
N1—H1C...Cl3 ⁱⁱⁱ	0.89	2.40	3.266 (4)	163
N2—H2A...Cl3 ⁱⁱⁱ	0.89	2.41	3.273 (4)	162
N2—H2B...Cl2	0.89	2.37	3.250 (3)	168
N2—H2C...Cl2 ^{iv}	0.89	2.79	3.528 (5)	142
N2—H2C...Cl4 ^{iv}	0.89	2.77	3.417 (3)	130

Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $1 - x, -y, 1 - z$; (iii) $x, y, z - 1$; (iv) $2 - x, -y, 1 - z$.

All H atoms were placed in calculated positions, with methyl C—H distances of 0.96 Å and N—H distances of 0.89 Å, and were refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(\text{parent atom})$.

Data collection: *CrysAlisCCD* (Oxford Diffraction Ltd, 2003); cell refinement: *CrysAlisCCD*; data reduction: *CrysAlisRED* (Oxford Diffraction Ltd, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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